Polarized Brillouin Scattering in Salol: Effects of Rotation-Translation Coupling

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We have studied the 90° VV-polarized Brillouin scattering spectrum of the molecular glassformer salol and observed a previously unnoticed VV-dip feature at low frequencies for temperatures above 300K. This new feature is a consequence of rotation-translation coupling, as recently predicted by Pick, Franosch *et al* [Eur. Phys. J. B **31**, 217, 229 (2003)], who showed its relationship to the Rytov dip that occurs in the corresponding VH spectrum. The analysis of the spectra shows good agreement with the theoretical predictions.

Thirty five years ago, the broad quasielastic rotational line in the depolarized $I_{VH}^{90}(\omega)$ light-scattering spectra of liquids composed of strongly anisotropic molecules was found to have a previously unknown feature [1], [2]. With high resolution, at temperatures above the melting point, a narrow central dip usually designated as the "Rytov dip" [3] is observed. For liquids that can be supercooled, with decreasing temperature the Rytov dip disappears, the rotational line narrows, and new spectral features develop symmetrically on the wings and, as the glass transition temperature is approached, sharpen to become the TA Brillouin components.

The origin of the Rytov dip was shown by Andersen and Pecora [4], [5] and others [6] to be rotation-translation [RT] coupling, the same phenomenon responsible for flow birefringence. While the rotational spectral line is generated by orientational fluctuations, the dynamics of these fluctuations are modified by coupling of orientation to the transverse velocity.

To explain the evolution of the VH spectrum with temperature, the equations of coupled translation-plus-rotation dynamics must be modified to include viscoelasticity, i.e. memory functions must be introduced for the relevant transport properties. This synthesis was first described in a series of papers by C.H. Wang and his coworkers who carried out light-scattering studies of a series of molecular glassforming liquids [7]. If memory effects are ignored, Wang's phenomenological theory reduces to the Andersen-Pecora results which were obtained from a two-variable Zwanzig-Mori formalism with the Markov approximation.

Dreyfus, Pick and their coworkers have carried out a new phenomenological analysis of the VH spectrum which is more complete than previous theories [8]. In their most recent publication, this analysis was extended to the polarized $I_{VV}^{90}(\omega)$ spectrum, and it was found that this spectrum should also exhibit a characteristic signa-

ture of RT coupling [9]. Franosch *et al* [10] implemented a parallel Zwanzig-Mori analysis of both the VH and VV spectra with results that agree with the phenomenological results of Dreyfus *et al* and, if memory effects are ignored, again recover the VH results of Andersen and Pecora.

In order to test these new theoretical results and, in particular, to search for the predicted new effect of RT coupling in the VV spectrum, we have carried out an extensive light-scattering study of the much-studied molecular glassforming liquid salol (T_M=316K, T_G=218K). We collected three complete sets of spectra, 90°VV, 90°VH, and VH backscattering, at 23 temperatures between 380K and 210K. A detailed analysis of all the spectra will be reported in a forthcoming publication [11]. In this communication we discuss the 90° VV spectra and describe the new feature we have observed that confirms the predictions of Pick, Franosch *et al* [9], [10]. In contrast to previous analyses of VV spectra which assumed simple addition of the rotational and density-fluctuation spectra, RT coupling must be included in the analysis.

In the phenomenological theory, the conventional equations of hydrodynamics are augmented with an additional non-hydrodynamic variable to describe the departure from isotropy of the average molecular orientation within a small volume element. For linear (or axially symmetric) molecules, if $P(\theta, \phi, \vec{r}, t)$ is the probability of finding a molecule at $\vec{r}$ with its axis $\hat{u}$ pointing in the direction (θ, ϕ), an appropriate variable is the orientational density which forms a symmetric traceless second-rank tensor $\bar{\bar{Q}}$:

$$Q_{ij}(\vec{r}, t) = \int d\theta d\phi P(\theta, \phi, \vec{r}, t) \left[\hat{u}_i(\theta, \phi)\hat{u}_j(\theta, \phi) - \frac{1}{3}\delta_{ij}\right]. \tag{1}$$

For the equation of motion of $\bar{\bar{Q}}$, Dreyfus and Pick used a damped harmonic oscillator equation

1

$$\frac{\partial^2}{\partial t^2}Q_{ij} = -\omega_R^2 Q_{ij} - \Gamma \otimes \frac{\partial}{\partial t}Q_{ij} + \Lambda'\mu \otimes \tau_{ij} \qquad (2)$$

where $\otimes$ denotes convolution, ω_R is a librational frequency, $\Gamma(t)$ is the orientational friction function, and the last term incorporates the coupling of orientation to the shear rate τ_{ij}.

In the Zwanzig-Mori approach, the damped oscillator equation for Q is obtained only if both Q and dQ/dt are included in the set of selected variables. (With Q alone, the equation of motion for Q is purely relaxational.) This result parallels the fact that both the density fluctuation ρ_q and its time derivative (or current) must be included to obtain the usual damped oscillator equation for the density-fluctuation (LA) modes.

The fluctuations of the dielectric tensor include two terms, one due to density fluctuations and the other to orientational fluctuations:

$$\delta\bar{\bar{\epsilon}}(\vec{r},t) = a\delta\rho_m(r,t)\,\bar{\bar{I}} + b\,\bar{\bar{Q}}\,(r,t) \qquad (3)$$

Both terms in Eq. (3) as well as their cross products must be evaluated to find the complete spectrum. The resulting equation for the VV-polarized spectrum $I_{VV}^{90}(\omega)$ obtained by Pick et al [9] (with some simplifying approximations [11]) is given by

$$I_{VV}(\omega) = \frac{I_0}{\omega}\mathcal{I}m\left\{\frac{4}{3}R(\omega) + \frac{q^2}{\rho_m}\Lambda\,[S + \frac{2}{3}R(\omega)]^2 P_L(\omega)\right\} \qquad (4)$$

where the initial $\frac{4}{3}R(\omega)$ term is the pure orientational part of the spectrum (which can be determined by analysing the VH backscattering spectra), Λ is the RT coupling coefficient, and $P_L(\omega)$ is the longitudinal propagator:
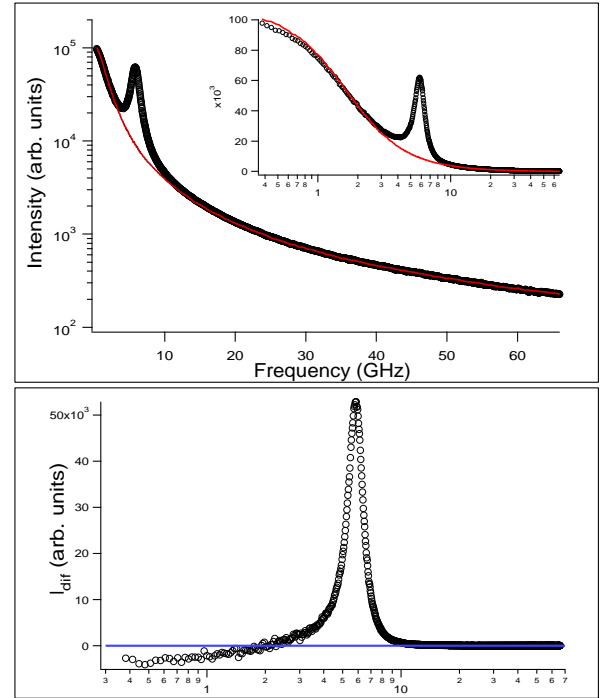
$$P_L(\omega) = \left\{\omega^2 - \omega_0^2 - i\omega\Gamma_0 - \frac{q^2}{\rho_m}\left[V\omega\eta_s(\omega) - \frac{4}{3}\Lambda\frac{R^2(\omega)}{1 - R(\omega)}\right]\right\}^{-1} \qquad (5)$$

In Eq. (5), the longitudinal viscosity $\eta_L(\omega)$ does not appear explicitly because we assume that it is proportional to the shear viscosity $\eta_S(\omega)$: $\eta_L(\omega) = V\eta_S(\omega)$, ω_0 is the bare LA frequency, and Γ_0 is a constant damping term due to other processes.

The RT coupling mechanism enters twice. First in Eq. (4) where the first term in the square brackets (S) represents the conventional light-scattering channel for LA modes via coupling of the dielectric constant to density fluctuations (the first term in Eq. (3)), while the second term represents an additional light scattering channel provided by coupling of the LA mode to molecular orientation. Second in Eq. (5) where the final term gives the reduction of the shear viscosity by a factor proportional to Λ. For salol, this reduction is $\sim 10\%$ and has only a minor effect on the shape of the spectrum.

Experiments: Salol samples for our light-scattering experiments were prepared by triple vacuum distillation of phenyl salicylate purchased from Sigma Chemical Company. The final distillation was made into cylindrical glass sample cells which were then flame sealed under vacuum. The Brillouin scattering experiments were performed with incident 5145 Å monomode laser excitation of ~ 250 mW; the spectra were measured with a Sandercock 6-pass tandem Fabry-Perot interferometer.

In Fig. 1, the upper panel shows the 350K VV spectrum (points) and the VH backscattering spectrum (solid line) scaled to overlap the VV spectrum at high frequencies (30-50GHz). Numerical subtraction of the two spectra yields the 350K difference spectrum $I_{dif}(\omega)$ shown by the points in the lower panel. For frequencies above $\simeq$ 15GHz, $I_{dif}(\omega)$ vanishes as expected. However, for

FIG. 1. Generating the $I_{\text{dif}}(\omega)$ difference spectra. Upper panel: I_{VV}^{90} spectrum (points) and scaled I_{VH}-back spectrum (line) for $T = 350$ K. Inset: same, with linear y and log x scales. Lower panel: the difference spectrum obtained by subtracting the scaled I_{VH}-back spectrum from the I_{VV}^{90} spectrum. (The line is I = 0)

frequencies $\leq 2GHz$, $I_{dif}(\omega) < 0$. As we will see, it is this negative region which is the signature of the new RT

2

coupling effect. $I_{dif}(\omega)$ is given by Eq. (4) with the pure orientation term suppressed:

$$I_{dif}(\omega) = \frac{I_0}{\omega}\mathcal{I}m\left\{\frac{q^2}{\rho_m}\Lambda\ [S + \frac{2}{3}R(\omega)]^2 P_L(\omega)\right\} \quad (6)$$

In the fits, we modeled $R(\omega) = R^0 H_R(\omega)$ and $\omega\eta_S(\omega) = \eta_S^0 H_S(\omega)$ with a "hybrid function"

$$H_x(\omega) = [1 - (1 + i\omega\tau_x)^{-\beta_x} + i\omega p_x(\tau_x^{-1} + i\omega)^{a-1}] \quad (7)$$

(where x = R or S) which combines the Cole-Davidson function at low frequencies with a ω^a power-law at high frequencies to approximate the mode-coupling form in the frequency region of the experiments [12]. The parameters in $H_R(\omega)$ were determined from the VH backscattering spectra, and those in $H_S(\omega)$ and Λ from the VH-90° spectra [11]. Both τ_R and τ_S increase rapidly with decreasing temperature with a nearly constant ratio.

Fits to the density-fluctuation-only model: In analyzing the spectra, we initially ignored RT coupling and fit the difference spectra with a conventional density-fluctuation-only model. If RT coupling is ignored, Eqs. (5) and (6) reduce to

$$I_{dif}(\omega) = \frac{A}{\omega}\mathcal{I}m[P_L(\omega)] \quad (8)$$

where $A = I_0(q^2/\rho_m)\Lambda S^2$, and

$$P_L(\omega) = \left[\omega^2 - \omega_0^2 - i\omega\Gamma_0 - \Delta^2 H_S(\omega)\right]^{-1} \quad (9)$$

where $H_S(\omega)$ is the hybrid function (Eq. [7]) for the shear viscosity $\eta_S(\omega) = \eta_S^\circ H_S(\omega)$ and $\Delta^2 = (q^2/\rho_m)V\eta_S^\circ$.

We fit the difference spectra to Eqs. (8) and (9), with the parameters appearing in $H_S(\omega)$ and Λ again fixed from the I_{VH}^{90} fits. This is a conventional analysis of Brillouin scattering spectra similar to that carried out previously for many other materials (e.g. refs. [13], [14].) In the fits, A, Δ^2, and ω_0 were the free parameters. We found that good fits could be obtained with fixed Γ_0 proportional to T, as was found for propylene carbonate [13]. The choice $\Gamma_0 = T/600$ was found to produce values of ω_0 quite close to the values computed from ultrasonic data. These "density-fluctuation-only" fits are shown in Fig. 2 by broken lines. While the fits are generally excellent, for temperatures above 280K the low-frequency regions of the fits become increasingly less satisfactory because the spectra become negative at low frequencies while the theoretical fits are always positive. (Note that while the difference spectra have low-frequency negative regions,
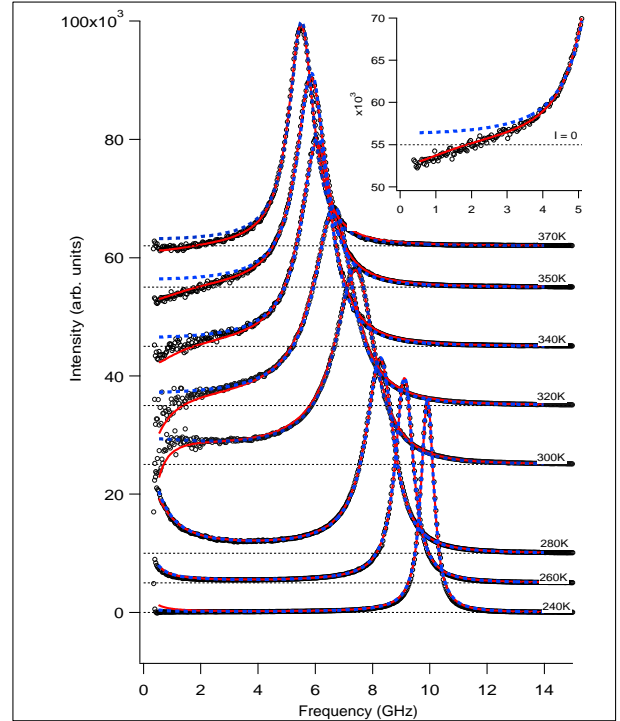

FIG. 2. Difference spectra for T =240, 260, 280, 300, 320, 340, 350, and 370K. The spectra have been scaled and shifted vertically for visibility. Solid lines: fits to the full theory; broken lines: fits to the density-fluctuation-only model. The dotted lines indicate the I=0 baseline for each spectrum. Inset: Low-frequency region for T = 350K.

the full $I_{VV}(\omega)$ spectra are everywhere positive).

Fits to the full theory: Next, we fit the $I_{dif}(\omega)$ spectra using the full theory of Eqs. (5) and (6) with ω_0, V, and S as the free fitting parameters. The fit results are shown in Fig. 2 where we have included both the full fits (solid lines) and the density-fluctuation-only fits (broken lines). At low temperatures the two fits are indistinguishable, showing that RT coupling is unimportant in the frequency range of our spectra. At higher temperatures, the low-frequency region is fit much better by the full theory than by the density-fluctuation-only theory, showing that RT coupling, which is ignored in the conventional density-fluctuation-only analysis, is the source of the negative region.

Referring to Fig. 4 in ref. [9], there is also a tendency for the full theory to fall below the density-fluctuation-only fits to it at low frequencies when $\omega_B\tau \simeq 1$. There are differences between the lineshapes in that figure and ours, however, which we attribute primarily to the use of a single relaxation time in their calculations, while for salol, $\tau_R \sim 15\tau_S$. Because of this large ratio, there is a clear separation between the Mountain mode visible as a positive feature at temperatures between 260 and 290K

3

and the VV dip, visible for temperatures above 300K. The Mountain mode results from coupling of strain to structural relaxation and, at low temperatures, is visible at frequencies below the Brillouin peak. For $T \geq 300$K, it is cut off at low frequencies by the VV dip.

Physically, RT coupling enters because the uniaxial strain that characterizes a longitudinal acoustic mode is a superposition of simple compression and shear strain. In liquids composed of anisotropic molecules, the fluctuating longitudinal strain induces a preferential orientation of the molecules in the plane perpendicular to $\vec{q} = q\hat{z}$, adding to $\delta\epsilon_{yy}$ which determines the VV scattered intensity. Referring to the equation of motion for Q (Eq. [2]), the steady-state solution gives Q_{ij} proportional to the strain rate τ_{ij}. Therefore, for oscillatory LA waves in the low-frequency limit (where $\omega\tau << 1$), if $\delta\rho_{ij}$ is real, then δQ_{ij} is imaginary. In this limit, the optical coupling function $C(\omega) = [S + (2/3)R(\omega)]^2$ in Eq. [6] becomes

$$[S + \frac{2}{3}R(\omega)]^2 \rightarrow [S + i\omega\frac{2}{3}R_0\beta_R\tau_R]^2 \approx [S^2 + i\omega\frac{4}{3}R_0\beta_R\tau_R] \tag{10}$$

and, from Eqs. [5] and [6] in this low-frequency limit,

$$I_{dif}(\omega) \rightarrow \frac{I_0 q^2 \Lambda}{\rho_m \omega_0^4}[S^2\eta_L\frac{q^2}{\rho_m} - S\omega_0^2\frac{4}{3}R_0\beta_R\tau_R] \tag{11}$$

The second term, being negative, reduces the intensity at low frequencies, but it will disappear at frequencies $\omega > \tau_R^{-1}$ where Q can no longer follow the oscillating strain. This reduction effect is similar to the Rytov dip where, for $\omega\tau_R << 1, R^2(\omega)$ is negative which adds a narrow negative component to the center of the broad rotational line.

We therefore conclude that the VV-dip phenomenon observed in this experiment is a consequence of RT coupling as described in the analysis of references [9] and [10]. Finally, we note that there have been many previous Brillouin-scattering studies of liquids of anisotropic molecules (including salol), where the VV-dip could have been observed. The reason that it has not been reported previously is suggested by the upper panel of Fig. 1 which shows that on a log plot, the low-frequency $I_{VV}^{90}(\omega)$ spectrum is very close to the rotational spectrum. It is only when the low-frequency region of the *difference spectrum* is examined that the small low-frequency VV dip becomes apparent. An extensive discussion of this conclusion together with the full underlying data analysis can be found in Ref [11].

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